Supporting Information

Design and Synthesis of Micron-Sized Spherical Aggregates Composed of Hollow Fe_2O_3 Nanospheres for Use in Lithium-Ion Batteries

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- XRD patterns of the powders (a) post-treated at 500 °C under H_2/Ar mixed gas atmosphere and (b) subsequent heat-treated at 300 °C under air atmosphere.
- XPS spectra of the powders: (a) O 1s spectrum of the Fe-carbon composite powders post-treated at 500 °C under H_2/Ar mixed gas atmosphere, (b) O 1s spectrum, and (c) Fe 2p spectrum of the hollow Fe_2O_3 nanosphere aggregates subsequent heat treated at 300 °C under air atmosphere.
- Thermal-analysis of hollow Fe_2O_3 nanosphere aggregates.
- Morphology and phase analysis of solid Fe_2O_3 powders prepared by spray pyrolysis: (a) SEM image and (b) XRD pattern

- (a) N_2 gas adsorption and desorption isotherms and pore size distribution of (b) solid Fe_2O_3 powders, and (c) hollow Fe_2O_3 nanosphere aggregates.
- SEM images of (a) solid Fe_2O_3 powders and (b) hollow Fe_2O_3 nanosphere aggregates obtained after first cycle.
- SEM images of (a) solid Fe_2O_3 powders and (b) hollow Fe_2O_3 nanosphere aggregates obtained after 100 cycles.
- TG analysis of Fe-carbon composite powders post-treated at 500 °C under H_2/Ar mixed gas atmosphere.
- Cyclic voltammetry (CV) curves of solid Fe_2O_3 powders for the first 7 cycles at a scan rate of 0.1 mV s^{-1}.

Experimental

Synthesis of hollow Fe_2O_3 nanosphere aggregates and solid Fe_2O_3 powder: The hollow Fe_2O_3 nanosphere aggregates were prepared with a three-step process. The iron oxide-carbon composite powder was prepared with spray pyrolysis using a spray solution of iron nitrate enneahydrate [$(Fe(NO_3)_3)\cdot 9H_2O$] and sucrose. In the spray pyrolysis system used, droplets were generated with a 1.7 MHz ultrasonic spray generator consisting of six vibrators. The droplets were carried to a quartz reactor (length = 1200 mm, diameter = 50 mm) by a carrier gas of N_2 at a flow rate of 7 $L\cdot min^{-1}$. The reactor temperature was maintained at 400 °C. The concentrations of iron nitrate enneahydrate and sucrose dissolved in distilled water to create the spray solution were 0.1 and 0.1 M, respectively. The first stage of the post-pyrolysis treatment involved heating the iron oxide-carbon composite powder to 500 °C under a 10% H_2/Ar reducing atmosphere for 10 h to produce the Fe-carbon composite powder. The second stage of the post-pyrolysis treatment involved heating the Fe-carbon composite powder to 300 °C under an oxidizing air atmosphere for 5 h to produce the hollow Fe_2O_3 nanosphere aggregates. For comparison purposes, a solid Fe_2O_3 powder was prepared directly with spray pyrolysis using a spray solution containing only iron nitrate enneahydrate (air atmosphere, temperature = 500 °C).

***Characterizations*:** The microstructure of the powders was observed with field emission scanning electron microscopy (SEM, Hitachi, S-4800) and field emission transmission electron microscopy (TEM, JEOL, JEM-2100F). In addition, their crystal structure was evaluated with X-ray diffraction (XRD, X'Pert PRO MPD) using Cu Kα radiation (λ = 1.5418 Å) at the Korea Basic Science Institute (Daegu). X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) with a focused monochromatic Al Kα at 12 kV and 20 mA was used to analyze the composition of the specimens. The surface area of the powders was determined with the Brunauer–Emmett–Teller (BET) method, using N_2 as the adsorbate gas. Thermogravimetric analysis (TGA) were performed with a Pyris 1 TGA (Perkin Elmer, temperature range = 25–650 °C, heating rate = 10 °C min^{-1}, static air atmosphere).

***Electrochemical Measurements*:** The electrochemical properties of the powders were analyzed by constructing 2032-type coin cells. The anode was prepared by mixing the active

material, carbon black, and polyacrylic acid (PAA) in a weight ratio of 7:2:1. Li metal and microporous polypropylene film were used as the counter electrode and separator, respectively. The electrolyte was created by dissolving 1 M of $LiPF_6$ in a mixture of fluoroethylene carbonate and dimethyl carbonate (FEC/DMC, 1:1 v/v). The discharge/charge characteristics of the samples were investigated by cycling over a potential range of 0.001–3 V at various current densities. Cyclic voltammograms were measured at a scan rate of 0.1 mV s^{-1}. The size of the Fe_2O_3 powders negative electrode was 1 cm × 1 cm and the mass loading was approximately 1.2 mg cm^{-2}.

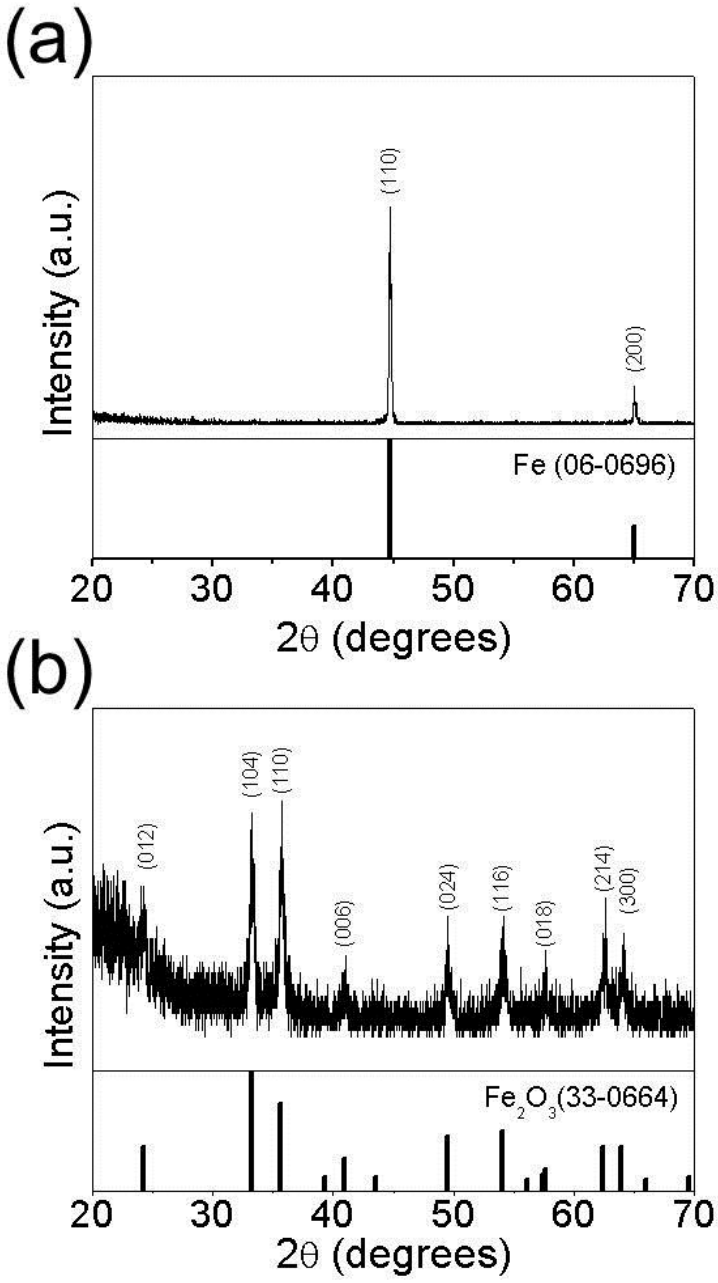

Figure S1. XRD patterns of the powders (a) post-treated at 500 °C under H_2/Ar mixed gas atmosphere and (b) subsequent heat-treated at 300 °C under air atmosphere.

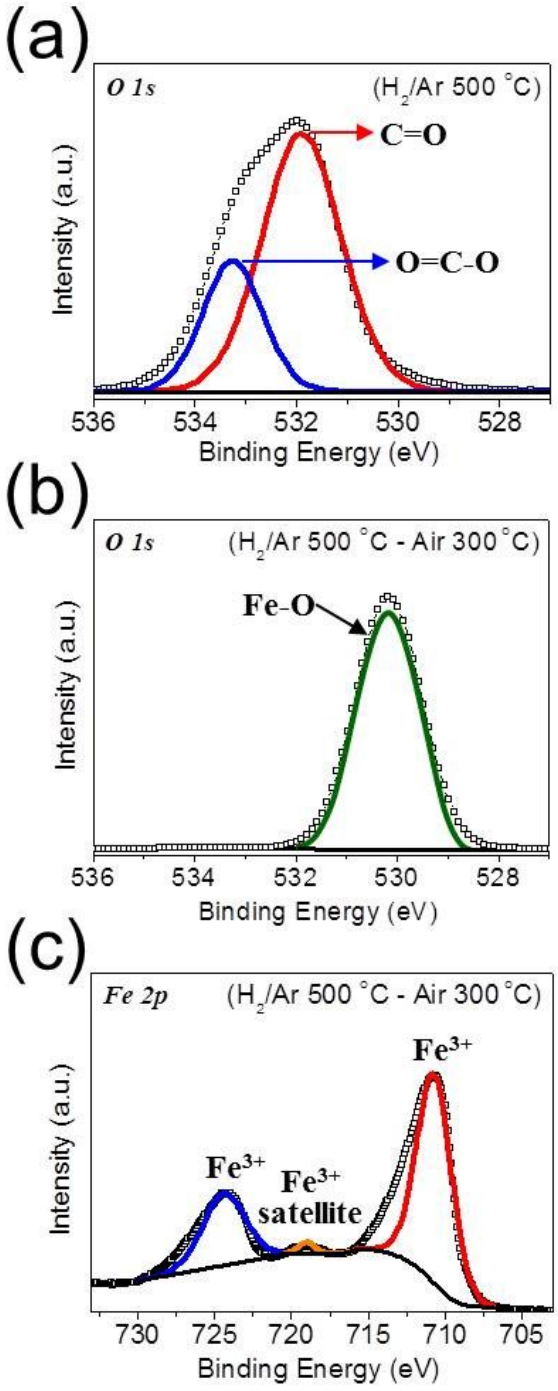

Figure S2. XPS spectra of the powders: (a) O 1s spectrum of the Fe-carbon composite powders post-treated at 500 °C under H_2/Ar mixed gas atmosphere, (b) O 1s and (c) Fe 2p spectra of the hollow Fe_2O_3 nanosphere aggregates subsequent heat treated at 300 °C under air atmosphere.

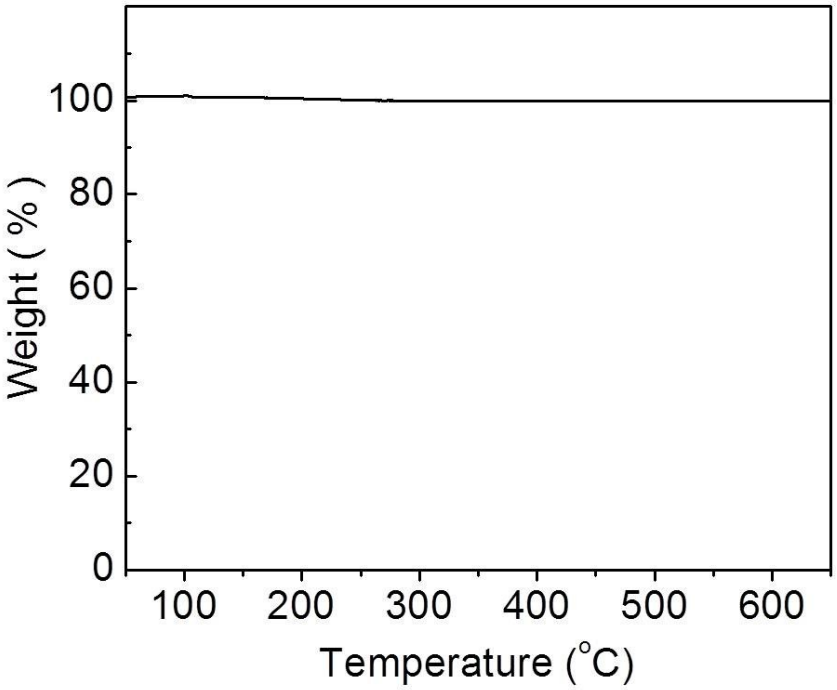

Figure S3. Thermogravimetric curve of the hollow Fe_2O_3 nanosphere aggregates.

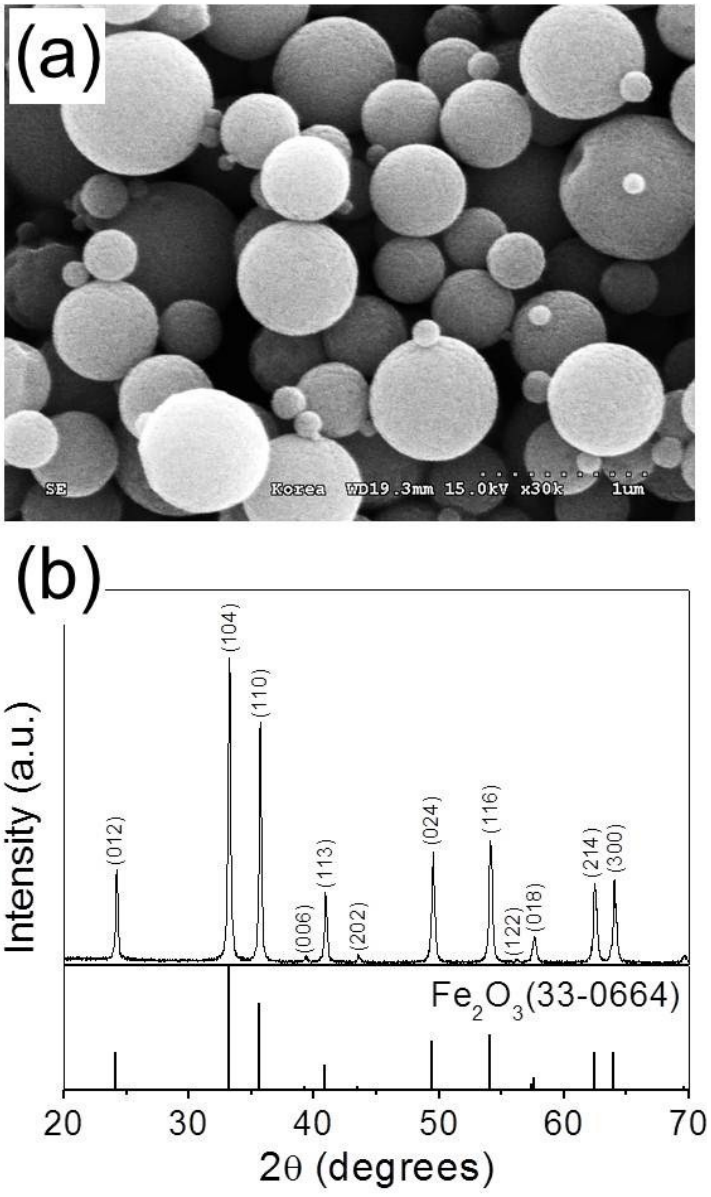

Figure S4. SEM image and XRD pattern of the solid Fe_2O_3 powders prepared by spray pyrolysis.

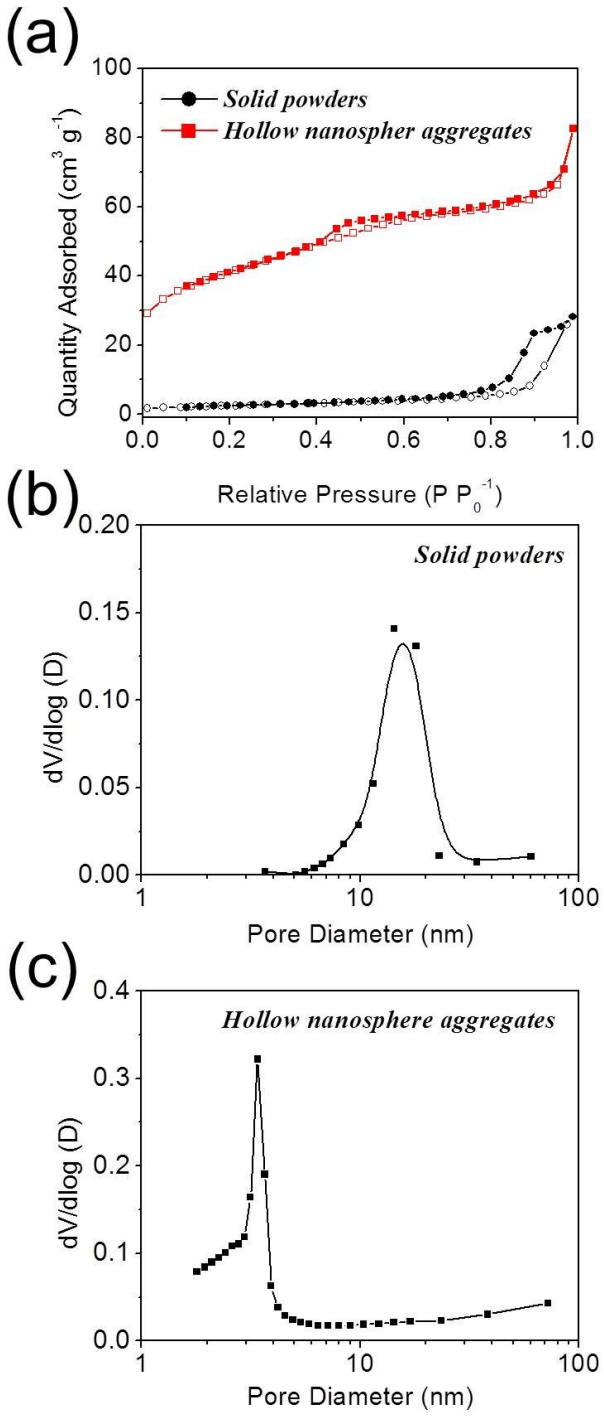

Figure S5. (a) N_2 gas adsorption and desorption isotherms and pore size distributions of (b) solid Fe_2O_3 powders, and (c) hollow Fe_2O_3 nanosphere aggregates.

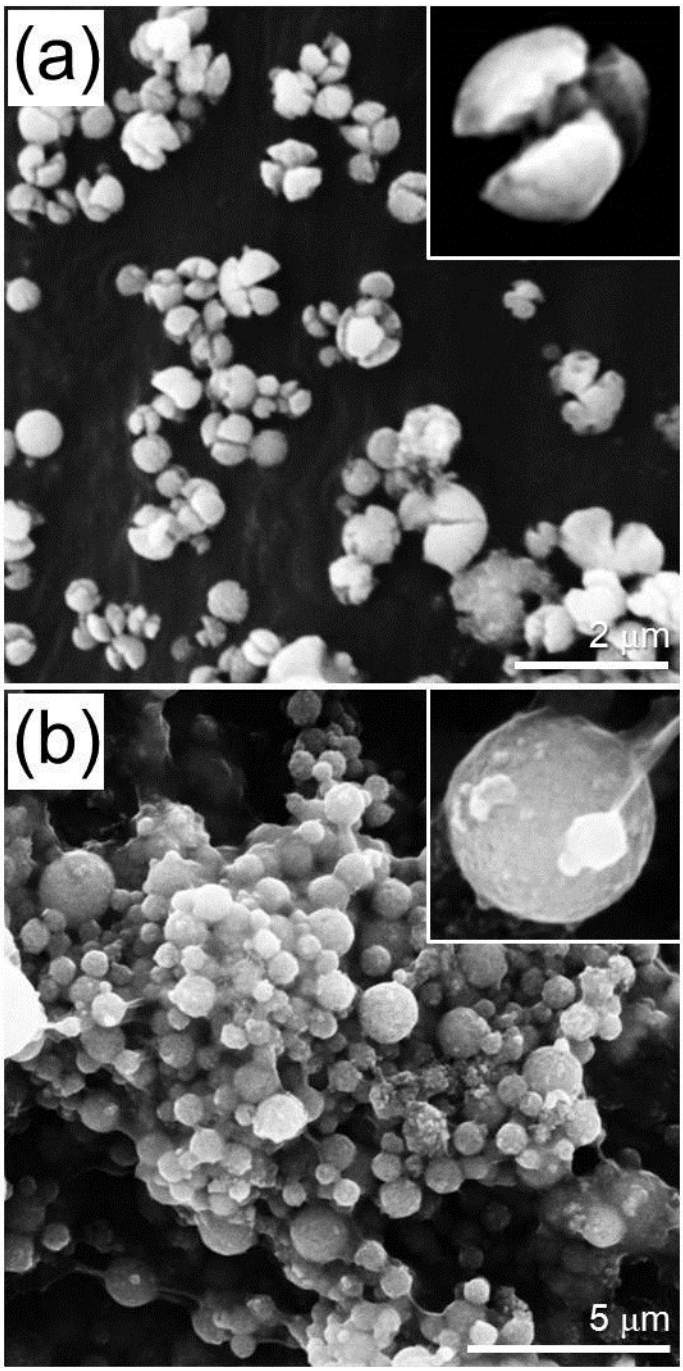

Figure S6. SEM images of (a) solid Fe_2O_3 powders and (b) hollow Fe_2O_3 nanosphere aggregates obtained after first cycle.

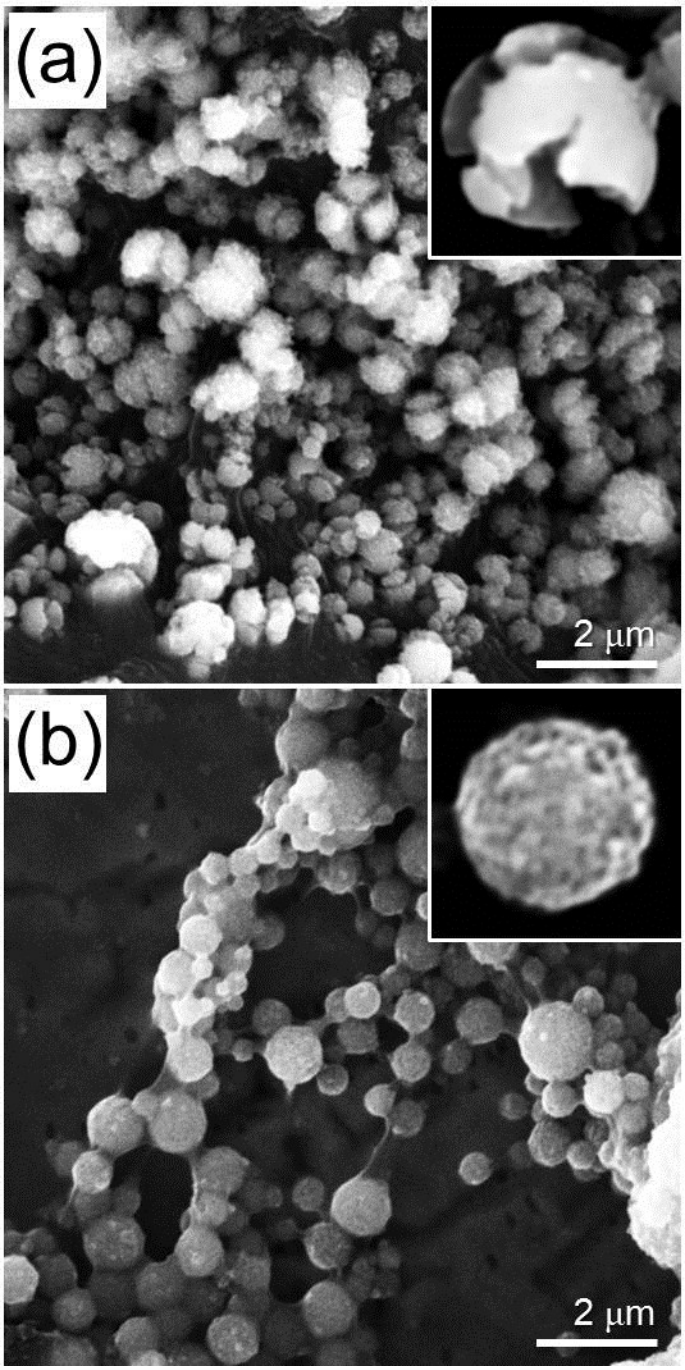

Figure S7. SEM images of (a) solid Fe_2O_3 powders and (b) hollow Fe_2O_3 nanosphere aggregates obtained after 100 cycles.

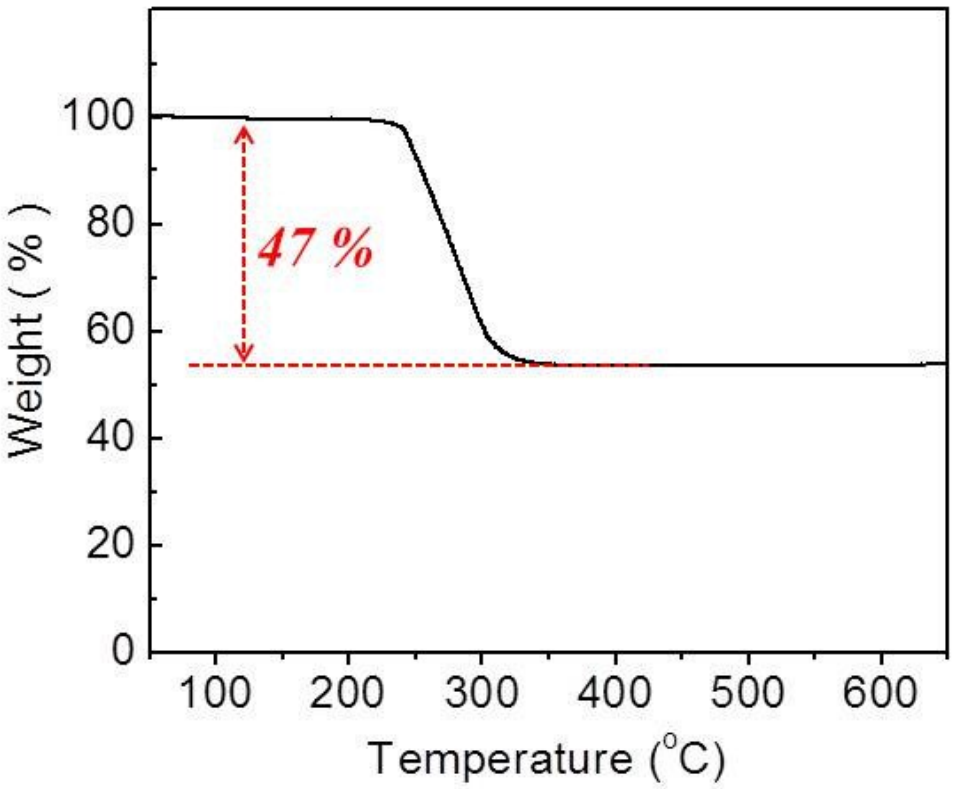

Figure S8. TG analysis of Fe-carbon composite powders post-treated at 500 °C under H_2/Ar mixed gas atmosphere.

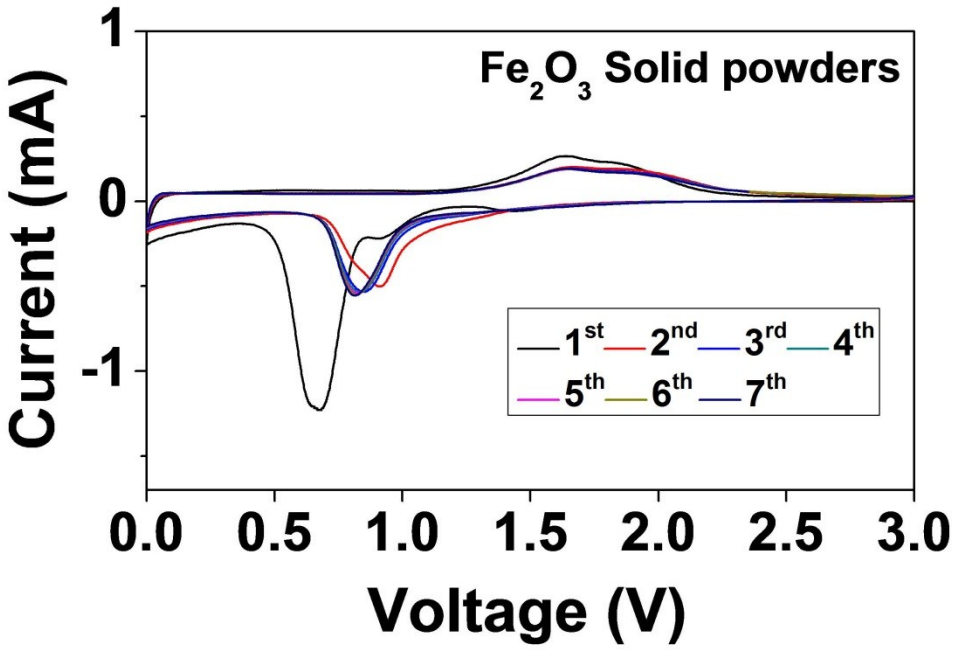

Fig. S9. Cyclic voltammetry (CV) curves of the solid Fe_2O_3 powders for the first 7 cycles at a scan rate of 0.1 mV s^{-1}.